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### (54) (METH)ACRYLIC ACID ESTER AND ITS PRODUCTION

(57)Abstract:

PURPOSE: To obtain a (meth)acrylic acid ester which is inexpensive and capable of being stably supplied and to provide a production method therefor.

CONSTITUTION: This invention provides a glycerol-saturated aliphatic acid and (meth)acrylic acid ester obtained by binding glyceryl group with a (meth)acrylic acid and a saturated aliphatic acid, a method for esterification of a glyceride with (meth)acrylic acid and/or (meth)acrylic acid derivative by the use of an immobilized lipase and a method for esterification of a higher alcohol with (meth)acrylic acid and/or (meth)acrylic acid derivative by the use of the immobilized lipase. The objective ester can be produced in a safe manner and at a low cost, has excellent functions and can be used as a paint, ink, tacky adhesive, adhesive, crosslinking agent or reactive component for film, etc., and rubber modifier.

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**DETAILED DESCRIPTION**

**[Detailed Description of the Invention]**

**[0001]**

**[Industrial Application]** This invention about the manufacturing method of acrylic acid (meta) (acrylic acid (meta) as used herein means acrylic acid and/or methacrylic acid) ester and (meta) acrylic ester. It is related with the manufacturing method of glycerin saturated fatty acid (meta) acrylic ester and glycerin (meta) acrylic ester, and the manufacturing method of alcoholic (meta) acrylic ester in detail.

**[0002]**

**[Description of the Prior Art]** The alcoholic (meta) acrylic ester conventionally produced by carrying out ester composition of acrylic acid (meta), or its derivative and higher alcohol, are very important as a monomer for compounding various industrial materials and the polymers which can change, since a vinyl group is held. The polymers polymer produced by carrying out copolymerization of this alcoholic (meta) acrylic ester to other monomers is used as cross linking agents, such as a paint, a binder, adhesives, and a film, and a reactant ingredient and a rubber modifier.

**[0003]** However, it has the fault that work environment causes an environmental public nuisance is easy to be polluted while requiring large-scale incidental facilities and space, since such alcoholic (meta) acrylic ester is [ the manufacturing method ] a chemosynthesis reaction which uses a chemical catalyzer. In order to use higher alcohol as a raw material, it has various faults -- material cost costs dearly, and also a reaction yield and the alcoholic (meta) acrylic ester itself which are produced by being low, therefore carrying out an ester synthetic reaction to these higher alcohol are dramatically expensive, and there is. Therefore, the cheap (meta) acrylic ester which has the same functionality was demanded.

**[0004]** On the other hand, although alcoholic fatty acid ester and fats and oils with a common ester synthetic reaction which uses lipase instead of are examined widely, [ the chemosynthesis reaction which uses a chemical catalyzer ] In the ester synthetic reaction using lipase, when acrylic acid is used for the substrate of a reaction, it is said that ester composition is not carried out (JP,60-227688,A specification). Then, although the manufacturing method of the alcoholic acrylic ester by an acrylic ester production bacillus was proposed, the alcohol which can be used as a raw material is limited to straight-chain-shape alcohol of the carbon numbers 1-8 (JP,60-227688,A specification).

**[0005]** The report that it was possible to manufacture alcoholic acrylic ester these days using fixed lipase furthermore was made (Ikeda, Tanaka, Suzuki et al., Tetrahedron Letters, Vol. 32, No.47, pp. 6865-6866, 1991). However, this method is an ester synthetic reaction which uses acrylic acid vinyl ester for a substrate, and in order that acetaldehyde may be produced as a reaction by-product and this may reduce the life of fixed lipase, it has the fault that the output yield per fixed lipase is low. The alcohol used as a substrate was also difficult for reaction efficiency falling remarkably and the number of carbon atoms using more nearly long-chain alcohol for a substrate in eight or more pieces.

**[0006]** It has been thought that it is impossible to manufacture alcoholic acrylic ester without using more nearly long-chain alcohol and branched chain-like alcohol and using a chemical catalyzer in today like the above.

**[0007]**

[Problem(s) to be Solved by the Invention] This invention provides the cheap (meta) acrylic ester which can be used as cross linking agents, such as a paint, a binder, adhesives, and a film, and a reactant ingredient and a rubber modifier.

The purpose is to provide the manufacturing method of the acrylic ester which is easy and can be manufactured with high yield (meta).

[0008]

[Means for Solving the Problem] As a result of inquiring wholeheartedly in view of a point on \*\*, glycerin saturated fatty acid acrylic ester which an acrylic acid group and a saturated fatty acid group combined with a glyceryl group this invention persons, Knowledge of having the same functionality as alcoholic (meta) acrylic ester which uses higher alcohol known conventionally was acquired. Knowledge that it was possible easy and to obtain acrylic ester (meta) with high yield was acquired by carrying out an ester synthetic reaction as a manufacturing method using fixed lipase. This invention is completed based on this knowledge.

[0009] Namely, this invention in any one or more positions of the 1st place – the 3rd place of a glyceryl group. (Meta). An acrylic acid group joins together and a saturated fatty acid group combines with other any one or more positions. . It is characterized by carrying out the ester synthetic reaction of glycerin saturated fatty acid (meta) acrylic ester and glycerin fatty acid ester; acrylic acid (meta), and/or (meta) the acrylic acid derivative using fixed lipase. A manufacturing method of glycerin fatty acid (meta) acrylic ester and 12 carbon atom – 22 piece alcohol, acrylic acid (meta), and/or (meta) an acrylic acid derivative, a manufacturing method of alcoholic (meta-) acrylic ester carrying out an ester synthetic reaction using fixed lipase — it comes out.

[0010] Hereafter, this invention is explained in full detail. First, the 1st invention in this invention is cross linking agents, such as a paint, a binder, adhesives, and a film, a reactant ingredient, and the glycerin saturated fatty acid (meta) acrylic ester that did not exist conventionally as acrylic ester which can be used as a rubber modifier (meta).

[0011] An acrylic acid group (meta) combines with any one or more positions of the 1st place – the 3rd place of a glyceryl group, and a saturated fatty acid group combines glycerin saturated fatty acid (meta) acrylic ester with other any one or more positions.

[0012] Unless a saturated fatty acid group has joined together, the flexibility of polymers polymer itself is low and the purpose of this invention cannot be attained. It is preferred that it is a range whose numbers of carbon atoms are two pieces – 22 pieces as such a saturated fatty acid acyl chain, and it is more preferred that it is a range whose number of carbon atoms is 12 pieces thru/or/, or 18 pieces further. Although it is preferred that it is straight chain shape as for these acyl chains, even if it is a branched chain-like, it is convenient in any way. Although these monomers are depended on a radical polymerization as a method of carrying out copolymerization in large quantities today, it is not desirable, in order that an active methylene group of this unsaturated fatty acid may check a radical polymerization as bonded fatty acid is unsaturated fatty acid.

[0013] Although it is glycerin saturated fatty acid (meta) acrylic ester which glycerin saturated fatty acid (meta) acrylic ester in this invention contains one or more vinyl groups of acrylic acid (meta) origin in one molecule of glycerin skeletons, and contains one or more saturated fatty acid groups, Even if a compound which three vinyl groups of acrylic acid (meta) origin contain in one molecule of glycerin skeletons, i.e., AKURIRIN etc., contains, it is convenient in any way. A little glycerin saturated fatty acid ester of substrate origin may remain. Therefore one saturated fatty acid group combined with which position of glycerin saturated fatty acid ester at one acrylic acid group (meta) and other positions, it can remain and one can also contain glycerin saturated fatty acid (meta) acrylic ester which is in a state of a hydroxyl group.

[0014] Since "plant and animal oil fat cheap as a raw material of glycerin saturated fatty acid ester or its hydrogenate oil and fat can be asked, this glycerin saturated fatty acid (meta) acrylic ester can be provided very cheaply compared with expensive higher alcohol.

[0015] An invention of the 2nd of this invention relates to a method of manufacturing glycerin fatty acid (meta) acrylic ester containing the above glycerin saturated fatty acid (meta) acrylic ester with easily and sufficient yield.

[0016] Glycerin fatty acid ester as a raw material for manufacturing glycerin fatty acid (meta) acrylic ester. It may be glycerin trifatty acid ester, i.e., triglyceride, and they may be \*\*\*\*\*-\*\* fatty acid ester, i.e., diglyceride, or glycerin mono- fatty acid ester, i.e., monoglyceride. They may be these mixtures. Therefore, as long as it comprises saturated fatty acid, triglyceride, i.e., fats and oils, which are the raw materials for manufacturing glycerin saturated fatty acid (meta) acrylic ester, the origin may be what kind of fats and oils, such as animality and a vegetable property. It is especially preferred that it is triglyceride of vegetable hydrogenate-oil-and-fat origin.

[0017] Although a polymerization in which acrylic ester which is a monomer (meta) carries out copolymerization to other monomers is a radical polymerization to which most was suitable for mass production in today, it is as having described above that bonded fatty acid must be saturated fatty acid in that case. However, when low production may be sufficient, it may be possible at anionic polymerization and bonded fatty acid may be unsaturated fatty acid in that case.

[0018] The ester synthetic reaction of such glycerin fatty acid ester, acrylic acid (meta), and/or (meta) the acrylic acid derivative is carried out. (Meta) As a derivative of acrylic acid, derivatives, such as methyl ester of acrylic acid (meta), ethyl ester, pro PIRURU ester, and butylester, can be used, for example.

[0019] It is as follows if an example of a manufacturing method of glycerin fatty acid (meta) acrylic ester is shown. First, fats and oils obtained from an oil seed, for example, a soybean, a palm, a palm core, a coconut, a corn, a cottonseed, etc. or those hardening fat, acrylic acid (meta), or its derivative is used as a substrate. It is manufactured by warming under existence of fixed lipase and polymerization inhibitor in a temperature requirement in which a reaction of fixed lipase is possible.

[0020] A reaction system is possible in any methods, such as a batch type and continuous system which passes a column.

[0021] Fixed lipase used for these ester exchange reactions, What is necessary is just to fix lipase enzyme to a publicly known carrier on physical, an ionic bond covalent bond target, etc., and glycerin fatty acid ester is received. It can be used if it is what acts at random, and a thing which has ester composition ability and ester interchange ability the 1st place even if it is any, although it acts on the 3rd place specifically. Although it is [ anything ] good as lipase used, a thing from microorganism is preferred and the origin has an Aspergillus, Rhizopus, a Mucor, the Candida group, etc.

[0022] A publicly known thing can be used for polymerization inhibitor used during these ester synthetic reactions in order to control that a compound which has a vinyl group starts a polymerization reaction. Especially, hydroquinone, hydroquinone monomethyl ether, etc. are preferred.

[0023] In these ester synthetic reactions, it can carry out if needed under existence of a suitable organic solvent used as a substrate of a reaction, for example, hexane, heptane, isooctane, etc.

[0024] In these ester synthetic reactions, a resultant at the time of using triglyceride for a substrate is acquired in the state of a mixture which acrylic acid 1 in substrate triglyceride and triglyceride substitution product, acrylic acid 2 in triglyceride substitution product, and acrylic acid 3 in triglyceride substitution product mixed. Although these glycerin fatty acid (meta) acrylic ester mixtures can be used for a polymerization reaction as they are after processing of removing polymerization inhibitor by a publicly known method, each compound can also be separated and used for them using a still more publicly known method.

[0025] Since the glycerin fatty acid (meta) acrylic ester in this invention can change the number of acrylic acid (meta) or chain length of fatty acid who joins together, it can grant character which suited a use to be used in the wide range. For example; acrylic acid 1 substitution product which one acrylic acid group in triglyceride replaced can form polymers of straight chain shape; when it polymerizes using this. Acrylic acid 2 substitution product which two acrylic acid groups in triglyceride replaced can form three-dimensional polymers which has the network structure, when it polymerizes using this. The flexibility of polymers produced by polymerizing by changing chain length of fatty acid which is a constituent can be adjusted.

[0026] Glycerin (meta) acrylic ester produced by making it above, As compared with alcoholic (meta) acrylic ester currently manufactured conventionally, it can manufacture very easily cheaply, and polymers polymer which obtained it by carrying out copolymerization of this can be effectively used

as cross linking agents, such as a paint, a binder, adhesives, and a film, a reactant ingredient, and a rubber modifier.

[0027]Next, the 3rd invention in this invention receives a manufacturing method of alcoholic (meta) acrylic ester manufactured by the chemosynthesis reaction which uses a catalyst conventionally. It is related with a method of manufacturing with very easily and sufficient yield by carrying out an ester synthetic reaction using fixed lipase.

[0028]Twelve carbon atom -22 piece alcohol is used for alcohol which is a raw material. The number of carbon atoms, 12/thru/or 18 alcohol which is especially easy to come to hand easily and cheaply is preferred. In this chain, two or more unsaturated double bonds may exist. Although it is preferred that it is straight chain shape as for a chain portion of alcohol, even if it is a branched chain-like, it is convenient in any way.

[0029]The ester synthetic reaction of alcohol of a more than, acrylic acid (meta), or its derivative is carried out using fixed lipase.

[0030]An ester synthetic reaction using fixed lipase can be carried out according to a manufacturing method of glycerin fatty acid (meta) acrylic ester shown previously.

[0031]It is the same as a case of manufacture of previous glycerin fatty acid (meta) acrylic ester that it can carry out under existence of a suitable organic solvent used as a substrate of a reaction in these ester synthetic reactions if needed.

[0032]

[Example]Hereafter, although an example explains the embodiment of this invention, this is illustration and the pneuma of the invention in this application is not restricted by these illustration. Each of parts and % means a weight reference among an example.

[0033]Example 1 agitating equipment, a thermostat, the column type bioreactor provided with the thermometer (using ene ZANOBA I (made by NGK Insulators, Ltd.)) One copy of fixed lipase (SP435 (made by NOVO)) was filled up with the mixed solution of 56 copies of hardening palm oil, and 44 copies of methyl acrylate, the column kept warm by the reaction temperature of 40 \*\* was made to pass it by rate-of-flow 5 ml/hr as a substrate, and reaction mixture was obtained.

[0034]It heated at 100 \*\* under decompression of reaction mixture, and distillation removal of the methyl acrylate was carried out from the inside of reaction mixture. It was made to cool, and after recovery, it newly mixed with hardening palm oil, and the removed methyl acrylate was used for the substrate. The reaction mixture from which methyl acrylate was removed was further heated at 250 \*\* under decompression, carried out distillation removal of the fatty acid methyl ester which is a by-product, and obtained the glycerin saturated fatty acid acrylic ester which is a resultant.

[0035]As a result of analyzing the glycerin saturated fatty acid acrylic ester which is this resultant using a high-speed fluid chroma TOGURAFISHI stem, the presentation of each triglyceride, In acrylic acid 1 in triglyceride substitution product, acrylic acid 2 in triglyceride substitution product was [ acrylic acid 3 in triglyceride substitution product ] 28.5% 44.0% 23.5% substrate triglyceride 4.0%.

[0036]The polymers produced by carrying out copolymerization of this resultant to the monomer of other polymerization nature, for example, methyl methacrylate, and methacrylic acid can be used for various resin materials as flexible, three-dimensional, dramatically high polymers which has the network structure.

[0037]In the Erlenmeyer flask sealed example 2, the mixture of 72 copies of inside chain length fatty acid triglyceride (MCT) of the carbon number 8, 28 copies of methyl acrylate, and one copy of fixed lipase (SP435 (made by NOVO)) is put as a substrate. After making it react for 24 hours, having kept it warm at 40 \*\* and stirring at any time using MAGUNE textile Thaler, suction filtration removed fixed lipase and reaction mixture was obtained.

[0038]The glycerin saturated fatty acid acrylic ester which is a resultant was obtained by removing methyl acrylate and fatty acid methyl ester using the same distillation removing method as Example 1.

[0039]As a result of analyzing the glycerin saturated fatty acid acrylic ester which is this resultant using a gas chromatography system, the presentation of each triglyceride, In acrylic acid 1 in triglyceride substitution product, acrylic acid 2 in triglyceride substitution product was [ acrylic acid 3 in triglyceride substitution product ] 6.0% 28.0% 42.5% substrate triglyceride 23.5%.

[0040]Acrylic acid 1 in triglyceride substitution product separated from this resultant. By carrying out copolymerization to the monomer of other polymerization nature, for example, methyl methacrylate, and methacrylic acid, the same character as what is obtained by copolymerization of alcoholic acrylic ester and the monomer of other polymerization nature is shown, and this copolymer can be used for various resin materials, such as a paint, a binder, and adhesives.

[0041]Using the mixed solution of 75 copies of stearyl alcohol, and 25 copies of acrylic acid as example 3 substrate, 100 copies of heptane were added to this, and reaction mixture was obtained by the same method as Example 2.

[0042]It heated under decompression of reaction mixture and azeotropic distillation removed the water which is a by-product out of reaction mixture with the heptane which is an azeotropy solvent. Distillation removal also of the acrylic acid was carried out simultaneously, and the alcoholic acrylic ester which is a resultant, i.e., acrylic acid stearyl, was obtained.

[0043]As a result of analyzing the alcoholic acrylic ester which is this resultant using a gas chromatography system, the presentation was stearyl alcohol 19.5% acrylic acid stearyl 80.5%.

[0044]This resultant can be used as cross linking agents, such as a paint, a binder, adhesives, and a film, or a reactant ingredient, and a rubber modifier like the acrylic acid stearyl obtained by the ester synthetic reaction which used the chemical catalyzer.

[0045]It was with 83 copies of soybean oil, and the mixed solution of 17 copies of methyl acrylate as example 4 substrate, and the glycerin acrylic ester which is a resultant was obtained by the same method as Example 1.

[0046]As a result of analyzing the glycerin acrylic ester which is this resultant using a high-speed fluid chroma TOGURAFISHI stem, the presentation of each triglyceride, In acrylic acid 1 in triglyceride substitution product, acrylic acid 2 in triglyceride substitution product was [ acrylic acid 3 in triglyceride substitution product ] 5.5% 27.5% 43.0% substrate triglyceride 24.0%.

[0047]This resultant forms a coat good under UV irradiation, when it uses for a paint individually, but the straight-chain-shape polymers which performed anionic polymerization to acrylic acid 1 in triglyceride substitution product which is an ingredient in this resultant can be dramatically used as drying good drying oil.

[0048]In the Erlenmeyer flask sealed example 5, the mixture of 83 copies of linseed oil, 17 copies of methyl acrylate, and one copy of fixed lipase (Lipozyme IM60 (made by NOVO)) is put as a substrate, After making it react for 24 hours; having kept it warm at 40 \*\* and stirring at any time using a magnetic stirrer, suction filtration removed fixed lipase and reaction mixture was obtained.

[0049]It heated at 100 \*\* under decompression of reaction mixture, and distillation removal of the methyl acrylate was carried out from the inside of reaction mixture. It was made to cool, and after recovery, it newly mixed with linseed oil and the removed methyl acrylate was used for the substrate. By this operation, the mixture of glycerin fatty acid acrylic ester and fatty acid methyl ester was obtained.

[0050]The mixture of the glycerin fatty acid acrylic ester which is this resultant, and fatty acid methyl ester, As a result of analyzing using a high-speed fluid chroma TOGURAFISHI stem, the presentation of each triglyceride in glycerin fatty acid acrylic ester, They were substrate saturated fatty acid triglyceride 32.7%, 45.9% of an acrylic acid 1 substitution-product thing in triglyceride originating in this, 21.4% of an acrylic acid 2 substitution-product thing in triglyceride, and 0.0% of an acrylic acid 3 substitution-product thing in triglyceride.

[0051]When it prints by having added this resultant to oil based ink and a printing surface is made to cover ultraviolet curing nature resin, as compared with the case where the oil based ink which does not add this resultant is used, binding of an ink portion and a coated resin portion can be strengthened, and coloring of paints can be improved.

[0052]

[Effect of the Invention]The glycerin saturated fatty acid (meta) acrylic ester of this invention can be rich in functionality, and can be used as cross linking agents, such as a paint, ink, a binder, adhesives, and a film; or a reactant ingredient, and a rubber modifier. The stimulativeness over the skin is very lower still, handling is easy, and it can supply cheaply and stably. The manufacturing method of acrylic ester can be cheaply performed very safely as compared with the case where the chemical catalyzer

of this invention performed under a severe reaction condition in some numbers (meta) since an ester synthetic reaction and an ester synthetic reaction can be mildly performed using an enzyme is used.

[Translation done.]

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**CLAIMS:**

[Claim(s)].

[Claim 1] Glycerin saturated fatty acid (meta) acrylic ester which an acrylic acid group (meta) combines with any one or more positions of the 1st place - the 3rd place of a glyceryl group, and a saturated fatty acid group combines with other any one or more positions.

[Claim 2] A manufacturing method of glycerin fatty acid (meta) acrylic ester carrying out the ester synthetic reaction of glycerin fatty acid ester, acrylic acid (meta), and/or (meta) the acrylic acid derivative using fixed lipase.

[Claim 3] A manufacturing method of alcoholic (meta) acrylic ester carrying out the ester synthetic reaction of alcohol, acrylic acid (meta), and/or (meta) an acrylic acid derivative of 12 carbon atom - 22 piece using fixed lipase.

[Claim 4] A way according to claim 3 the number of carbon atoms of alcohol is 12 pieces thru/or/, or 18 pieces.

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[Translation done.]